Title: OXYGEN – NOT JUST FOR BREATHING ANYMORE

Subhead: Oxygen Improves our Lives in Many Ways. Committee G-4 is Working to Ensure that it is used Safely.

Oxygen, the most plentiful substance in the earth's crust, was discovered in 1772 by Swedish chemist Carl Wilhelm Scheele. For about the first hundred years, oxygen was used solely for scientific purposes. Over the next hundred years, the modern oxygen industry developed. The history of the industry can be traced to the development of the refrigeration machine. The journey from that point to today's oxygen production industry involved such diverse subjects as the Paris theater, the brewing industry, explosives, and the ASTM Committee G-4.

Heading: TURNING AIR INTO A LIQUID

The commercial production of oxygen relies on the separation of air into its two primary constituents – oxygen and nitrogen. The genesis of air-separation technology can be traced to the work of Carl von Linde (figure 1). Linde, a professor at the Technical University at Munich (Germany), performed research and obtained patents on refrigeration cycles. His company, Gesellschaft fur Lindes Eismaschinen AG (later abbreviated to Linde AG), started building ammonia-driven refrigeration machines for breweries and ice houses in 1879. By 1891 Linde AG had built approximately 1,000 of these machines throughout Europe.

As a scientific endeavor, Linde became interested in producing lower temperatures by the refrigeration cycle and decided to try to liquefy air to achieve these results. Linde developed a prototype liquid-air machine consisting of a compressor, a heat exchanger, and an expansion valve. The heat exchanger was simply a 1,300 kg. spiral wound coil made by inserting 100 meters of 1 ½" pipe inside a section of 4" pipe (figure 2). He demonstrated the machine in May of 1895 by producing 3 liters of liquid air per hour. On June 5, 1895, the German Patent Office issued a patent to Carl Linde for "a process for the liquefaction of air and other gases."

At the time of Linde's patent there were no commercial applications for liquid air; however, Linde envisioned some potential applications – as a method to produce low temperatures for scientific experiments and as a way to produce explosives by combining oxygen-rich liquid air with highly reactive materials. Air Liquide, a French company that quickly followed Linde AG's entrance into the liquid air production business, identified another early application. One of their customers was a Paris theater that used liquid air to produce fog for their productions.

Heading: THE BIRTH OF AN INDUSTRY

Despite the existence of these possible uses for liquid air, the most viable and potentially lucrative application was as a precursor for the production of oxygen. In 1895, the year Linde received his patent, there were several companies that produced oxygen commercially; however, the demand was limited and the methods of production - via chemical reactions or electrolysis - were inefficient. In that same year Henri Le Chatelier, a French chemist discovered that the use of gaseous oxygen (GOX) with acetylene produced a much hotter flame than with air. Several years later in 1901, a design for an acetylene torch to weld and cut steel was patented. These developments spurred the demand for oxygen. This was a fortuitous set of circumstances for Linde, since in that same year Linde AG opened the world's first air separation plant in Munich, Germany. Linde AG also formed a partnership with several established companies,

which were producing oxygen by chemical methods, thus developing a customer base virtually overnight.

The Linde plant produced gaseous oxygen for commercial sale by exploiting the difference in boiling points between oxygen and nitrogen. Although more efficient than the chemical or electrolytic processes, this method was still very inefficient and the oxygen produced was of lower purity than oxygen produced by the other processes. Linde had been working on improving the method of separating oxygen from liquid air since he invented the liquid air machine, and in 1902, he developed a single column distillation method to extract liquid oxygen (LOX) from liquid air.

The next several years witnessed several significant innovations in liquid air production and oxygen extraction primarily by a Frenchman named Georges Claude. By the 1930's inventor and entrepreneur Paul Heylandt had perfected the design for a large piston expansion engine and constructed approximately 130 plants using this technology. Heylandt also promoted the concept of distributing oxygen in the liquid phase and developed several designs for dewars and other vessels to store and transport LOX (figure 3).

Heading: MAKING USE OF OXYGEN

In the early 1900's oxygen was primarily used with acetylene for cutting and welding operations. By the 1930s the largest demand for oxygen was for coal liquefaction, a process primarily used by the Germans to produce gasoline from coal. Several innovations in the steel production industry caused demand for oxygen to significantly increase in the 1950's. Over the next decade the demand for oxygen escalated as new medical devices, industrial processes, and environmental applications were developed to take advantage of the chemical properties of oxygen. In addition many manufacturing and chemical processes which had relied on the use of air as an oxidant were modified to use oxygen and as a result the efficiency of these operations was significantly improved. From the 1960's to the present, the space industry became a high profile user of oxygen as an oxidizer for rocket propulsion systems.

Heading: THE DANGEROUS SIDE

The oxidizing characteristics which make oxygen so useful in a variety of applications also make it very dangerous. The use of pure oxygen or even oxygen-enriched air results in an increased risk of ignition of materials and a more rapid combustion reaction should an ignition occur. Some materials that do not normally burn in air will burn in pure oxygen. Most materials including most metals will burn aggressively in high pressure (>1,000 psig) pure oxygen (figure 4).

The early oxygen producers understood the highly reactive nature of oxygen and performed research into the compatibility of common system materials with oxygen. These material testing efforts, which were in place by the early 1920's, utilized scientific tests developed by chemists to determine intrinsic material properties such as autogenous ignition temperatures or heats of combustion. An example of an early testing effort involved an industry committee formed in 1921 to investigate oxygen fires as referenced in a paper by *John K. Mabbs of the Linde Air Products Company*. Processes for designing, cleaning, assembling, and operating systems were developed by the oxygen producers through trial and error and experience and through limited interactions within the oxygen industry.

In the first half-century of the industry, there are very few records of any significant incidents caused by oxygen fires or explosions; however, common sense would lead one to believe that incidents resulting in injuries and deaths did occur but were attributed to other causes or were not publicly disclosed. In the subsequent decade, the 1960's, there were many recorded oxygen related explosions or fires, perhaps signaling an increased awareness of the danger of oxygen systems. The following are a few examples:

1. An oxygen main condenser explosion occurred in April, 1960, at a plant in West Virginia resulting in $1,000,000 in damage.
2. In February, 1961, explosions occurred in three filters in an oxygen plant in Louisiana.
3. In June, 1961, an oxygen booster compressor fire occurred at an oxygen plant in Michigan resulting in three fatalities.
4. In May, 1963, an oxygen tank truck overturned in Michigan. Initially the fire only involved the truck tires and gasoline; however, in a short time oxygen vapors greatly intensified the fire. There were no injuries.
5. An oxygen plant explosion occurred in Cleveland, in November, 1963, resulting in seventy-one days of plant downtime at a cost of $400,000. Fortunately there were no injuries.
6. In December, 1964, an oxygen booster compressor fire occurred at an oxygen plant in Texas. Again, fortunately no one was injured.

Heading: HEADLINE DISASTERS

In the 1960's there were also two very publicized major catastrophes – an explosion at a Linde AG plant in Dortmund, Germany and a fire which occurred during ground testing of the Apollo One capsule.

The 1961 Dortmund explosion resulted in fifteen fatalities and caused extensive damage to the plant (figure 5). The fire was attributed to the ignition of LOX-saturated charcoal in the sub-floor of the plant. The charcoal was thought to have been caused by welding slag produced by repairs performed during a plant shutdown. The slag most likely fell in the cracks between the stainless steel plates covering the wooden floor and initiated a small fire, which went unnoticed. Several days later LOX leaked onto the floor and saturated the charcoal, producing a very powerful contact explosive. In fact charcoal was one of the materials Linde AG intended to use to produce explosives by combining it with oxygen-rich liquid air. An ignition source as simple as the impact of a worker's foot could have initiated the explosion.

On January 27, 1967, a fire occurred in the Apollo One lunar module during a ground test sequence (figure 6). The capsule was pressurized with 16.7 psia gaseous oxygen at the time which caused the fire to spread rapidly. The three astronauts aboard, Virgil "Gus" Grissom, Edward White, and Roger Chaffee, were killed by carbon monoxide asphyxiation. Twenty-seven members of the support crew were treated for smoke inhalation, and two were hospitalized. The fire, which originated in a wire bundle near Grissom, was attributed to the ignition of insulation material by an electrical arc in one of the wires. As a result of the fire the amount and location of combustible materials in the Command Module were severely restricted and controlled.

The Dortmund and Apollo One incidents reinforced the need for a more comprehensive effort in the area of design and operation of oxygen systems. In order to

be effective this effort would have to include the standardization of equipment and practices and the testing of materials for oxygen applications.

Heading: STANDARDIZATION

The decade following the Apollo One fire witnessed the development of oxygen-related standardization efforts in Europe and the United States. The main organizations involved were the European Industrial Gases Association (EIGA) and the British Compressed Gas Association (BCGA) in Europe and the International Fire Protection Association (IFPA) and Compressed Gas Association (CGA) in the United States. These organizations focused their efforts on the design of oxygen-related equipment, the handling of oxygen, and the operation of oxygen systems. Examples of typical topics of these standards are bulk LOX storage, centrifugal compressor design, and the design and operation of GOX piping systems.

Heading: MATERIAL TESTING

At the same time several organizations were heavily involved in testing materials for use in oxygen service. In the United States the National Aeronautics and Space Administration (NASA) began placing a greater emphasis on oxygen compatibility testing as a direct result of the Apollo One incident and in preparation for the Space Shuttle program. In Germany the Bundesanstalt fur Materialprufung (commonly known as BAM) had been performing oxygen material compatibility testing for years. In both Europe and the United States, oxygen-producing companies such as Linde AG, Air Liquide, the British Oxygen Company (BOC), Praxair, and Air Products and Chemicals, Inc. had been involved in oxygen compatibility testing as well.

The test methods being used by these facilities were one of two types - standard chemical property tests (such as the bomb calorimeter test to determine heats of combustion) or tests that were specifically developed to determine ignition or flammability properties (such as NASA's mechanical impact test). Chemical test methods had been established for many years and in general are rather independent of test configuration. Other test methods were being conducted at one or more locations without standardization and thus the data could not be shared by different organizations or compared between facilities.

Heading: COMMITTEE G-4 FORMED

In 1973, Dr. Abraham Lapin of Air Products and Chemicals, Inc. became involved with a CGA task force on selecting materials for oxygen service and realized the difficulty in the application of data from non-standard tests. As a result he began to investigate the possibility of forming an organization to focus on materials selection for oxygen service. He was joined in this effort by other oxygen practitioners from BOC, NASA, and L'Air Liquide. Through their efforts the ASTM Committee G-4 on the Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres was formed. The immediate intention of the committee was to concentrate on test methods. The scope as narrated in the February 18, 1975 minutes was more expansive:

> "The development and promulgation of standard test methods, definitions, recommended practices and classifications for determining the compatibility/sensitivity of materials and materials configurations and applications intended for use in systems subjected to enriched oxygen atmospheres, taking into consideration, but not limited to, ignition, combustion, offgassing and reaction products and decomposition tendencies. The committee

will also concern itself with the promotion and dissemination of knowledge related thereto. This committee will coordinate its activities with other ASTM committees and other organizations having mutual interests."

The original membership, which numbered sixty-six, represented oxygen producers and users, system and equipment designers, and manufacturers of related products. The attendance list for the organizational meeting reflects membership from all levels of industry and government - presidents and vice presidents of companies, managers of every sort, research scientists, engineers, and salesmen.

Heading: G-4 ACHIEVEMENTS

The first significant accomplishment of Committee G-4 was the development of the Guide for Evaluating Materials for Oxygen Service (G-63) in June, 1980. The document provided the first and only existing standardized method for selecting non-metallic materials for oxygen service. Both the autoignition test (G-72) and the pneumatic impact test (G-74) were issued in 1982. During the subsequent twenty-five years, the committee has developed an additional seventeen standards on the subject of oxygen compatibility. Key standards include a design guide (G-88), a metals selection guide (G-94), a guide for controlling hazards and risks (G-128), and a failure analysis guide (G-145).

In March, 1982, Committee G-4 held its first international symposium in Phoenix, Arizona. In the ensuing sixteen years seven additional symposia were held in the United States and Europe culminating in the latest symposium in San Diego, CA, in November, 1997. Papers from the symposia can be found in the ASTM Special Technical Publications (STP) series. The subjects presented cover a wide range of areas including system design, failure analyses, research topics, test method results, literature surveys, and many others. The common denominator is their relevance to the field of oxygen compatibility or oxygen-enriched atmospheres.

In 1985 an education subcommittee was created to coordinate the development of a Special Technical Training course on oxygen compatibility. The course was developed and approved by the committee. The training, first offered in the late 1980's, has been taught almost one-hundred times throughout the United States, Europe, Australia, and Canada to approximately 1,500 attendees. The course involves real world oxygen incidents such as this astronaut suit fire (figure 7) to emphasize the importance of testing and analysis. This course has been the primary mechanism for the promotion and dissemination of knowledge involving oxygen compatibility as described in the committee scope.

In the mid-1980's an industry sponsored test program was conducted by the committee to perform the testing necessary for the creation of the metals selection guide (G-94). An additional metals testing program, developed to meet industry concerns, was initiated in 1995 and completed in 1998.

The Montreal Protocol, signed in 1987, detailed the international phase-out of ozone depleting substances which were and still are used mainly as refrigerants and solvents. Unfortunately several of the banned substances were solvents traditionally used to clean and verify oxygen systems. Thus Committee G-4 began developing cleaning and verification processes for oxygen systems which did not utilize these solvents and eventually hosted a symposium on the topic in Miami, Florida, on November 19 and 20, 1992. The papers presented at the conference were compiled and published as ASTM STP 1181.

Heading: G-4 ENTERS COMPUTER AGE

Technology has changed dramatically since Linde produced oxygen in the late 19th century, and within the last five years Committee G-4 has developed ways to use the power of computers and the internet for implementing the scope of the committee. The committee balloted and released a utilities disk with relevant software and membership data. Distribution of the G-4 News, the committee newsletter, was conducted via email providing more timely information while saving the committee money. Committee G-4 established a website which can now be found at http://www.wstf.nasa.gov/oxcompat/default.htm. In the future the committee is planning to establish an internet-based database to serve as a resource for oxygen-industry practitioners.

Heading: LOOKING FORWARD

Several new challenges face the committee as we approach the next millenium. One involves the development of new test methods and the application of existing methods for the design of oxygen systems at higher pressures and flow rates than existing systems. Probably the most important effort is the education of people on the hazards involved with oxygen or oxygen-enriched air as their use is becoming more commonplace in the medical and diving industries where there has been little or no training.

Even though it's the most common element in the earth's crust, oxygen in its pure form is a highly reactive substance. During its twenty-three years of existence, the work of Committee G-4 has contributed significantly toward the safe design and operation of oxygen and oxygen-enriched systems. The oxygen industry has made significant advances since its discovery over 225 years ago; however, as newer applications for oxygen are developed, the role of Committee G-4 in developing standards and educating oxygen practitioners will only increase.

Title: JURASSIC BIOSPHERE?

Subtitle: Some Scientists Believe a Real Jurassic Park Would Require a Controlled Atmosphere.

What would a forty foot long, 12,000 pound Tyrannosaurus do if it were somehow transported to your neighborhood? According to scientists at the 1993 meeting of the Geological Society of America, instead of snacking on the neighborhood children, the animal would gasp for air and eventually asphyxiate. The reason according to the researchers is that dinosaurs wouldn't be able to survive on the oxygen level found in today's atmosphere. This claim is the cornerstone of a theory which attempts to explain the gradual decline of dinosaur diversity over a period of several million years, culminating in their demise about 65 million years ago. It also introduces an interesting premise for speculation on the nature of the dinosaurs' environment if the underlying hypothesis regarding their atmosphere is valid.

Rich Hengst, a physiologist from Purdue University-Northcentral, provided evidence for the claim that the dinosaurs were not equipped to breathe our air. By studying a skeleton of Apatosaurus, the dinosaur previously known as Brontosaurus, Hengst deduced that it would have been virtually impossible for the 30 ton animal, which lacked a diaphragm for breathing, to take in an adequate amount of oxygen through its tiny nostrils by breathing air with only 21% oxygen. Thus he concluded that the atmosphere of the late Jurassic period, from which the Apatosaurus hails, must have contained a much higher concentration of oxygen than the air today. Other scientists have pointed to the enormous size of flying insects during the dinosaurs' time as additional proof of an increased oxygen level. This hypothesis is of particular interest to the members of ASTM Committee G-4, since the study of oxygen-enriched environments is the main reason for the committee's existence.

Gary Landis, from the U.S. Geological Survey, found supporting evidence for this hypothesis in a most unlikely place – fossilized tree sap, otherwise known as amber. Depicted in the movie Jurassic Park for entombing prehistoric insects, amber also trapped and preserved ancient air bubbles for millions of years. Landis' analysis indicated that the oxygen content of the air from 2 million years before the end of the Cretaceous Period (about 67 million years ago) to just after the end of the Period fell from 35% to 28%. Coincidentally the drop in oxygen content observed correlates well with the disappearance of dinosaurs from the fossil record.

The theory maintains that large quantities of carbon dioxide were produced by volcanic activity associated with the formation of the continents. These high carbon dioxide levels produced an abundance of plant life during the reign of the dinosaurs. At the same time a larger portion of the earth was covered with water than at present. The plant life produced vast amounts of oxygen. The oxygen that would have otherwise been partially consumed by bacteria feeding on dead organic material was not consumed because much of this material became covered by water. These circumstances resulted in a very high oxygen level in the atmosphere which was sustained for many millions of

years. The dinosaurs evolved and adapted to this environment until certain factors, which include a significant drop in sea levels and a dramatic increase in volcanic activity, resulted in a sudden drop in the oxygen concentration causing the gradual decline and ultimate demise of the dinosaur population.

Assuming the validity of this theory or merely the veracity of Landis' estimation of the prehistoric atmosphere raises many interesting questions concerning the effects of such an oxygen-rich atmosphere on the world of the dinosaur. Based on the present day knowledge of the flammability of materials in oxygen-rich atmospheres, we can assume that one consequence of the atmosphere on the planet would involve the frequency and intensity of fires. Forest fires caused by lightening would have happened much more frequently and burned with much greater intensity than those which occur today. The fires that recently devastated the East Coast of Florida, for example, would have been much more destructive and difficult to extinguish had they occurred in an atmosphere containing 35% oxygen. Some protection from the ignition or propagation of these prehistoric fires might have been provided by a greater amount of rainfall and a swamp or rainforest environment that were potential features of the dinosaurs' world.

Could ancient dinosaurs survive in our world? Unless scientists use genetic manipulation to create one, we may never know; however, if the atmosphere contained 35% oxygen it would certainly be difficult for us to survive in their world. Not only would we have to avoid being devoured by the enormous carnivores, but we would also have to worry about the prospect of ravenous fires. Given such a scenario, the work of ASTM Committee G-4 might have been as important seventy million years ago as it is today.

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